Mat. Res. Soc. Symp. Proc. Vol. 735 © 2003 Materials Research Society

Simulation of chiral liquid crystal self-assembly: analogies with the structural formation of biological fibrous composites

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ABSTRACT

The wide majority of biological fibrous composites exhibit twisted plywood architectures (planar or cylindrical) for mechanical reasons [1-5]. These supramolecular organizations originate from the passage of the extracellular matrix (surrounding the chiral fibrous molecules) trough a lyotropic cholesteric liquid crystalline mesophase during the structure formation process [1-5]. In this work, we used the well-established Landau-de Gennes theory of liquid crystals in order to develop a fundamental understanding of the supramolecular self-assembly process leading to the planar monodomain (defect-free) twisted plywood architecture [6]. Simulations illustrate the importance of constraining surface in the formation of defect-free (mechanically effective) composites. These results provide a better understanding of tissue morphogenesis which is highly desirable for the development of new bio-inspired synthetic composites.

INTRODUCTION

Nature produces composites with mechanical properties far beyond to those engineers are currently able to manufacture synthetically [7]. These materials are assembled at ambient temperature and pressure in aqueous environment while made of relatively simple and biodegradable constituents [7]. Given these advantages, natural composites are of a growing interest in applied material science. A major challenge in the field is to produce a synthetic equivalent of these materials. In order to do so, the structure formation process needs to be thoroughly described and understood.

Most of the biological fibrous composites have laminated structures called twisted plywoods. In these supramolecular assemblies, fibers are grouped in parallel and form superimposed sheets. The orientation of the fibers is uniform in each of the sheets but slowly changes by a small constant angle trough the thickness of the material. The twisted plywood architecture of biological fibrous composites is responsible for series of arced patterns and periodic extinction of light when seen in cross-section cuts under electron microscopy and polarized light respectively [1-5].

The origin of this organization is the passage of the extracellular matrix (forming the composite) surrounding the chiral fibrous molecules through a lyotropic cholesteric mesophase during the structure formation process and its successive crystallization. This temporary liquid crystalline state of the matrix provides the structural macromolecules with the necessary mobility to self-assemble in the twisted plywood fashion. This spontaneous helical packing at high concentration originates principally from a thermodynamical need for a minimal excluded volume between the long asymmetric molecules [1-6].

It is well-known that to be mechanically effective the twisted plywood architecture needs to be monodomain or in other words to be defect-free [1,6]. The way this achieved in the extracellular matrix forming the composite material represents the subject of this paper. Since the structure of liquid crystalline materials is recognized to be molded by its surroundings, Neville has formulated the hypothesis according to which, to be monodomain, the planar twisted plywood architecture needs a pre-crystallized constraining layer [1,6]. The mesophase is therefore trapped between this layer and the surface of the secreting cells. In absence of this restraining surface, the material is expected to exhibits a polydomain structure containing a network of defects and multiple helical directions [1,6].

This work aims to verify this hypothesis by simulating the spontaneous self-assembly process occurring in the material. The microstructure evolution is captured by a mathematical model based on the well-established Landau-de Gennes theory of liquid crystals.

THEORY AND GOVERNING EQUATIONS

The structure of the material is described by a second-order tensor **Q**, known as the tensor order parameter, which is based on the second moment of the orientation distribution function. This macroscopic quantity that enables us to describe unambiguously the long-range orientational order, in its more general format, reads [8]:

$$\mathbf{Q} = \mathrm{S}\left(\mathbf{nn} - \frac{\boldsymbol{\delta}}{3}\right) + \frac{1}{3}\mathrm{P}\left(\mathbf{mm} - \mathbf{ll}\right), \tag{1a}$$

where the following restrictions apply:

$$\mathbf{Q} = \mathbf{Q}^{\mathrm{T}}; \qquad \mathrm{tr}(\mathbf{Q}) = 0; \qquad -\frac{1}{2} \le \mathrm{S} \le 1; \qquad -\frac{3}{2} \le \mathrm{P} \le \frac{3}{2}; \tag{1b, c, d, e}$$

$$\mathbf{n}\cdot\mathbf{n} = \mathbf{m}\cdot\mathbf{m} = \mathbf{l}\cdot\mathbf{l} = 1; \qquad \mathbf{nn} + \mathbf{mm} + \mathbf{ll} = \boldsymbol{\delta}. \tag{1f, g}$$

The unit vectors **n**, **m** and **l** present in Eqs. (1a, f, g) form an orthogonal director triad which characterizes the orientation of the phase. The unit vector **n** is known as the uniaxial director, and **m** and **l** as biaxial directors. The quantities S and P, which are respectively known as uniaxial and biaxial scalar order parameters, are measures of molecular alignment. The uniaxial scalar order parameter gives the degree of alignment along the uniaxial director **n** while the biaxial scalar order parameter gives the degree of alignment along the first biaxial director **m**. The scalar order parameters and the tensor order parameter **Q** (main frame) are given by:

$$\mathrm{S} = \frac{3}{2}\left(\mathbf{n}\cdot\mathbf{Q}\cdot\mathbf{n}\right); \qquad \mathrm{P} = \frac{3}{2}\left(\mathbf{m}\cdot\mathbf{Q}\cdot\mathbf{m} - \mathbf{l}\cdot\mathbf{Q}\cdot\mathbf{l}\right). \tag{2a, b}$$

$$\mathbf{Q} = \begin{bmatrix} -\frac{1}{3}(\mathrm{S}-\mathrm{P}) & 0 & 0 \\ 0 & -\frac{1}{3}(\mathrm{S}+\mathrm{P}) & 0 \\ 0 & 0 & \frac{2}{3}\mathrm{S} \end{bmatrix} \tag{2c}$$

The tensor order parameter **Q** characterizes thoroughly the microstructure of the phase by combining information about orientation and alignment. Its quadrupolar symmetry retains the usual head-tail invariance that implies equivalence between the director field **n** and **–n**. The

correspondence between phase and alignment are: isotropic (S=0, P=0), uniaxial (S≠0, P=0) and biaxial (S≠0, P≠0).

The Landau-de Gennes phenomenological theory expresses the free energy of a liquid crystalline material by a power series expansion of scalar invariants of the tensor order parameter **Q** and its gradients ∇**Q**. The energy expression is made of a short-range contribution describing the phase transition phenomenon and a long-range contribution describing elastic force balance. In the absence of external fields, the total dimensionless free energy of the lyotropic mesophase reads [8,9]:

$$f = f_{is} + f_{sr} + f_{lr}, \tag{3a}$$

$$f_{sr} = \frac{1}{2}\left(1-\frac{U}{3}\right)\mathrm{tr}(\mathbf{Q}^2) - \frac{U}{3}\mathrm{tr}(\mathbf{Q}^3) + \frac{U}{4}\left[\mathrm{tr}(\mathbf{Q}^2)\right]^2, \tag{3b}$$

$$f_{lr} = \frac{1}{2}\left\{\left(\left(\frac{\xi}{h_0}\right)(\nabla\times\mathbf{Q}) + 4\pi\left(\frac{\xi}{p_0}\right)\mathbf{Q}\right)^2 + \upsilon\left(\left(\frac{\xi}{h_0}\right)(\nabla\cdot\mathbf{Q})\right)^2\right\}, \tag{3c}$$

where f_{is} is the free energy of the isotropic state; f_{sr} and f_{lr} are respectively the short and long-range contribution to the total free energy density f. The parameter U is the thermodynamic potential, proportional to the concentration of asymmetric rod-like molecules, which drives the phase-transition; ξ is a coherence length characterizing the distance over which variations of long-range orientational order can occur (this length furnishes, in turns, the order of magnitude of a defect size); h_0 is an geometric length giving the thickness of the material sample; p_0 is the pitch of the cholesteric liquid crystalline material. The remaining parameter υ symbolizes a measure of the elastic anisotropic in the material.

The time evolution of the tensor order parameter **Q** follows the standard gradient flow equation [10]:

$$-\gamma(\mathbf{Q})\frac{\partial\mathbf{Q}}{\partial t} = \frac{\delta f}{\delta\mathbf{Q}} = \left[\frac{\partial f}{\partial\mathbf{Q}} - \nabla\cdot\frac{\partial f}{\partial\nabla\mathbf{Q}}\right]^{[s]}, \qquad \gamma(\mathbf{Q}) = \left(1-\frac{3}{2}\mathrm{tr}(\mathbf{Q}^2)\right)^2, \tag{4a, b}$$

where the superscript [s] denotes symmetric and traceless tensors, and where $\gamma(\mathbf{Q})$ is a rotational viscosity. The dimensionless governing equation **Q**=**Q**(r,t) for the spatiotemporal evolution of the tensor order parameter is given as follows:

$$-\gamma(\mathbf{Q})\frac{\partial\mathbf{Q}}{\partial t} = SR + LR, \tag{5a}$$

$$SR = \left(1-\frac{U}{3}\right)\mathbf{Q} - U(\mathbf{Q}\cdot\mathbf{Q})^{[s]} + U(\mathbf{Q}:\mathbf{Q})\mathbf{Q}, \tag{5b}$$

$$\begin{aligned} LR = &-\left(\frac{\xi}{h_0}\right)^2\left\{\nabla^2\mathbf{Q} - \left[\nabla\cdot(\nabla\mathbf{Q})^T\right]^{[s]} + \upsilon\left[\nabla(\nabla\cdot\mathbf{Q})\right]^{[s]}\right\} \\ &+\left(\frac{\xi}{h_0}\right)\left(\frac{\xi}{p_0}\right)\left[-8\pi(\nabla\times\mathbf{Q})\right]^{[s]} \\ &+\left(\frac{\xi}{p_0}\right)^2\left[-16\pi^2\mathbf{Q}\right]. \end{aligned} \tag{5c}$$

The tensors SR and LR represent the short and long-range contributions to the dynamics of **Q**. The coupling parameter ξ/h_0 control the balance between short and long-range effects while ξ/p_0

controls the balance between chiral and achiral effects. In the limit $\xi/p_0 \rightarrow 0$, the material describes an achiral ordinary nematic liquid crystalline material.

RESULTS AND DISCUSSIONS

In all our simulations, the liquid crystalline material is initially considered to be in a stable isotropic phase. This disordered state corresponds to a low concentration of chiral molecules in the surrounding extracellular matrix of the biological composite. Within our framework, this initial isotropic state is described by a field of tensor whose eigenvectors are randomly oriented in space and whose eigenvalues are close to zero. Figure 1 depicts this state of randomness by showing the orientation of the main eigenvectors of **Q** (the director **n**).

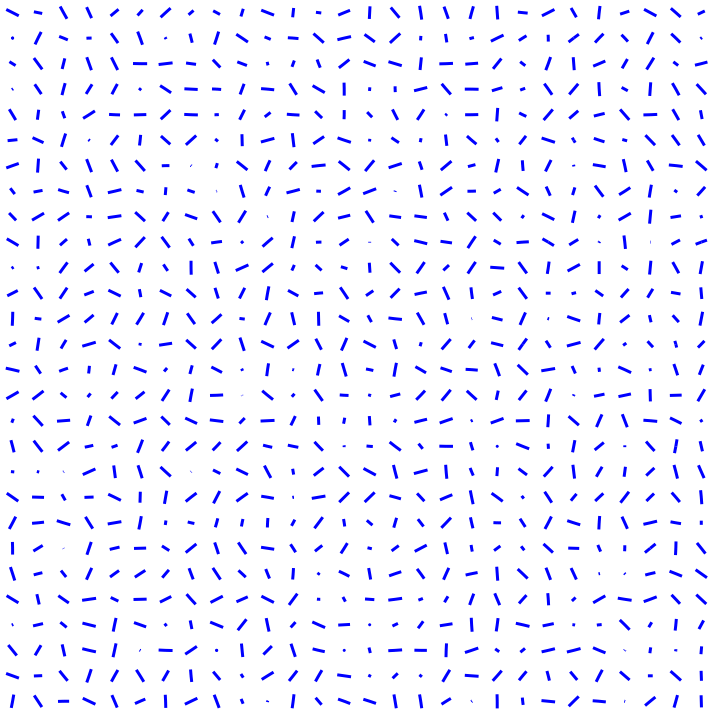

Figure 1. Representation of the initial isotropic state of the material (director field, **n**(r,t=0)).

In order to investigate the importance of restraining surfaces in the structure formation process of the biological composite, we first look at what happens in the absence of constrains. The influence of physical boundaries on the material bulk is annihilated by the following periodic boundary conditions:

$$\mathbf{Q}(x=0)=\mathbf{Q}(x=1);\quad \left.\frac{\partial \mathbf{Q}}{\partial x}\right|_{x=0}=\left.\frac{\partial \mathbf{Q}}{\partial x}\right|_{x=1};\quad \mathbf{Q}(y=0)=\mathbf{Q}(y=1);\quad \left.\frac{\partial \mathbf{Q}}{\partial y}\right|_{y=0}=\left.\frac{\partial \mathbf{Q}}{\partial y}\right|_{y=1}. \qquad (6a, b, c, d)$$

The ordering process starts as the concentration of chiral molecules in the matrix suddenly augments and that the initial isotropic state becomes unstable. It follows that orientation and order change so as to produce a new stable structure. Figure 2 shows the steady-state microstructure of the lyotropic liquid crystalline material using the director field representation.

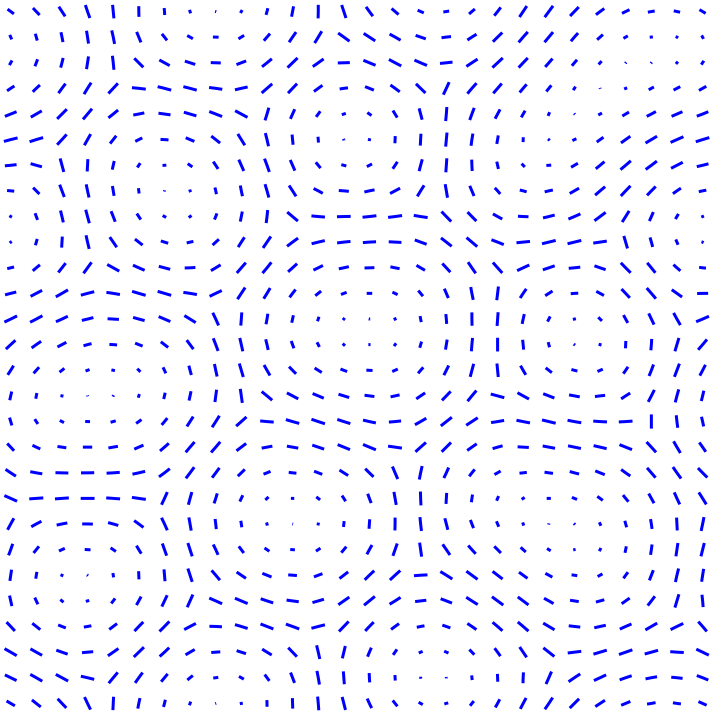

Figure 2. Steady-state microstructure when the composite material is not subject to any constraining surfaces.

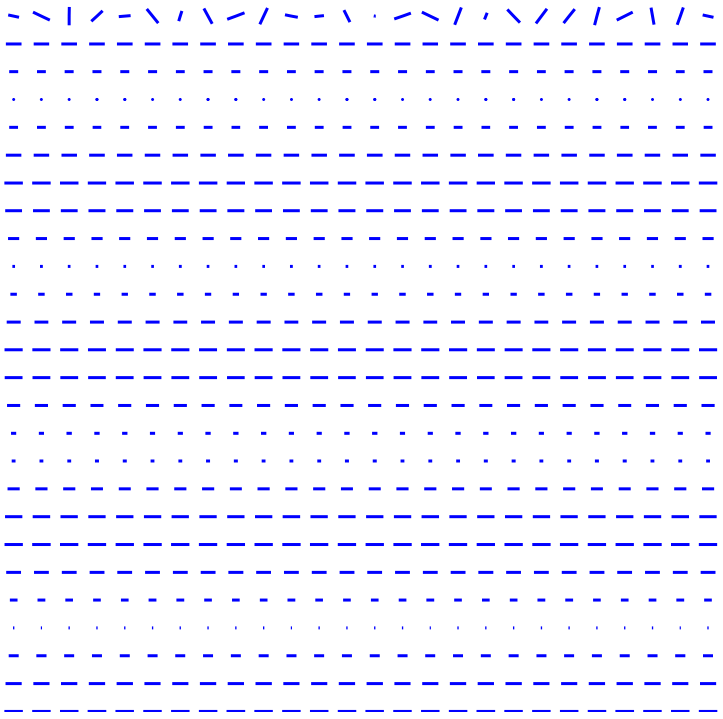

Figure 3. Steady-state microstructure when the composite material is subjected to a smooth constraining surface.

The structure displays multiple helical directions giving rise to a polydomain structure. The domains are interconnected by a network of defects (orientational incompatibilities between neighboring molecular directions). We next look at what happens in the presence of a pre-solidified ordered layer acting on the material bulk. Figure 3 show the steady-state average preferred molecular orientation in the material. The structure possesses a single helical direction that is normal to the restraining layer and consequently exhibits the planar monodomain twisted plywood architecture which is found in biological fibrous composites.

CONCLUSIONS

A model based on the well-established Landau-de Gennes theory of liquid crystal has been used to investigate the importance of constraining surfaces in the structural development of biological composites. The model is able to verify the hypothesis of Neville according to which a constraining layer is required for the structure to be monodomain and therefore mechanically effective [1,6,11]. The helical axis of the material is found to be normal to the restraining surface. In absence of such physical information the material is likely to display multiple helical directions which give a polydomain texture with defects weakening the material. These results encourage the evidence for the presence of constraining surfaces in biological fibrous composites and go towards a better understanding of structural transformations in these materials which are of primary interest for biomimetics purposes.

ACKNOLEDGEMENTS

This work is supported by the Air Force Office of Scientific Research, Mathematical and Space Science Program.

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